

METHODS OF MANUFACTURING POLISHING SUBSTRATES

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2025 RELEASE UNDER E.O. 14176

1 METHODS OF MANUFACTURING POLISHING SUBSTRATES

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4 Field of the Invention

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6 This invention relates to reaction molding and to
7 polishing pads for use in manufacturing semiconductor
8 devices such as wafers or memory disc substrates.

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10 Background of the Invention

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12 Many industries require the ability to efficiently
13 polish highly finished surfaces used in the semiconductor
14 and disc industry. Specific articles having highly
15 finished surfaces include, but are not limited to,
16 semiconductor/silicon wafers and memory disc substrates.

17 Presently, the method of polishing silicon wafers utilizes
18 polishing pads made from felts saturated with urethanes,
19 which have been polymerized to form a rigid surface.

20 Although these devices are highly useful and efficient in
21 polishing highly finished surfaces, they are difficult to
22 manufacture and it is difficult to control their quality
23 during the manufacturing process. The variations that
24 exist from pad to pad are systemic to the saturation

1 process and it is very difficult to produce large numbers
2 of polishing pads with predictable quality and performance
3 characteristics.

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5 Thus, there is a need for new and improved methods of
6 manufacturing polishing pads that are inexpensive, highly
7 efficient, and that produce durable compositions having
8 extremely predictable quality and performance
9 characteristics.

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Summary of the Invention

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3 The above problems and others are at least partially
4 solved and the above purposes and others realized in
5 reaction molding processes for manufacturing polishing pad
6 substrates. A reaction molding process of the invention
7 includes disposing a reaction mixture into a reaction mold
8 and then applying pressure and temperature to the reaction
9 mixture sufficient to cause polymerization and substrate
10 formation. In accordance with the principle of the
11 invention, the reaction mixture consists of polyvinyl
12 alcohol and a dibasic acid with a suitable catalytic cross-
13 linking agent. In another embodiment, the reaction mixture
14 consists of polyvinyl alcohol and an amine with a suitable
15 catalytic cross-linking agent. In yet another embodiment,
16 the reaction mixture consists of mixtures of both dibasic
17 acids and amines with polyvinyl alcohol and a suitable
18 catalytic cross-linking agent. The reaction pressure
19 preferably falls within a range of 10,000-20,000 pounds per
20 square inch (PSI) and the reaction temperature preferably
21 falls within a range of 100-200°C. A polishing pad
22 substrate formed by the reaction molding process of the
23 invention is mildly hard with a typical durometer reading
24 between 90 and 55 Shore D scale and exhibits a mildly waxy

1 surface and, in accordance with the invention, is useful
2 for polishing highly finished surfaces. Prior to the
3 reaction, the reaction mixture is capable of being
4 fortified with one or more polishing agents, one or more
5 fillers for controlling modulus and/or coefficient of
6 expansion of the reaction process, and/or a selected
7 quantity of one or more hydroxylated polymers and/or one or
8 more catalytic cross-linking agents. The reagents of the
9 reaction mixture can be layered in order to produce useful
10 zones of reaction, depending upon the polishing performance
11 characteristics desired of the substrate.

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1 DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT
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3 Reacting a dibasic acid, such as adipic acid, with an
4 alcohol or other hydroxylated polymer under a pressure in a
5 range of 10,000-20,000 pounds per square inch (PSI) and a
6 temperature in a range of 100-200°C, in the presence of a
7 suitable catalyst, produces a polymer having the following
8 structure: HOOC- $\overset{|}{(\text{CH}_2)_4}$ -COOH + -[CH₂-CHOH]_n- → H₂O + HOOC-
9 $\overset{|}{(\text{CH}_2)_4}$ -COO-CH-CH₂-
10 Prosecuting the foregoing reaction with
11 the additional reactant polyvinyl alcohol (PVA), produces a
12 polymer, which exhibits a mildly hard and waxy surface
13 which is useful as a polishing pad for producing highly
14 finished surfaces. The characteristics of the polymer are
15 capable of being altered by the addition of one or more
16 polishing agents such as aluminum oxide, silica, cerium
17 oxide or combinations of several agents, to produce
18 characteristics required to polish substrates to a highly
19 finished surface. These polishing agents can be classified
20 as polyesters.

21 Reacting a polybasic acid with urea in the presence of
22 a hydroxylated polymer such as PVA produces a mixture of
23 polymers consisting of polyester/polyamides having
24 structures as described above, in addition to the formation

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1 of urethanized polymers having the following structure: $\text{H}_2\text{N}-$
2 $\text{CO}-\text{NH}_2 + \text{HOOC}-(\text{CH}_2)_4-\text{COOH} + \text{PVA} \rightarrow n\text{H}_2\text{O} + \text{NH}_2\text{CO}-\text{NH}-\text{OC}-(\text{CH}_2)_4-$
3 $\text{COOH} + -[\text{CH}_2-\text{CH}-\text{O}(\text{CO}-\text{NH}_2)]_n-$. Depending on the particular
4 dibasic acid being used, the amine, and hydroxylated
5 polymer, the resulting hardness of the polishing pad
6 substrate is capable of being varied in order to meet
7 specific polishing needs. Other such dibasic acids are,
8 for example, azelaic acid, malonic acid, succinic acid and
9 certain lactones. Primary and secondary amines can also be
10 used to change the polishing characteristics when
11 urethanization takes place upon the hydroxylated polymer,
12 for example with PVA.

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14 In accordance with the invention, a quantity of
15 dibasic acid, a quantity of PVA and a quantity of urea are
16 mixed together with a suitable catalyst to form a reaction
17 mixture, which is disposed into a reaction mold. To the
18 reaction mixture are added various polishing agents, if
19 desired. The mold is closed and the reaction mixture
20 subjected to high pressure and temperature causing
21 polymerization to take place. These physical conditions
22 cause polymerization to take place forming a polishing
23 substrate. The various components of the reaction mixture
24 can be laid down in layers in the mold, in accordance with

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1 an embodiment of the invention. An example of this is
2 disposing a mounting layer of PVA and a cross-linking
3 catalyst on the bottom of the mold and mounting on the
4 mounting layer a polishing layer consisting of the
5 remaining reactants of the reaction mixture including the
6 polishing agents and catalyst in addition to, if desired, a
7 plasticizer, polyethylene glycol, ethylene glycol, etc., in
8 addition to other various polishing agents such as cerium
9 oxide, feldspar, silica, etc. A surfactant can also be
10 used in the polishing layer for facilitating distribution
11 of the polishing layer as it is cross-linked during the
12 molding process. At this point, the mold is closed and the
13 layered substrate subjected to high pressure and
14 temperature. These physical conditions cause
15 polymerization to take place in all the layers with
16 specific polymers grown in zones. This growth zone
17 polymerization forms the basic polishing pad substrate.
18 The zones are chemically attached to one another producing
19 inseparable zones, each having unique chemical and physical
20 characteristics. In a typical example, the polishing layer
21 can consist of 2-5% by weight of a plasticizer, 25-60% by
22 weight of a polishing agent, 1-2% by weight of a
23 surfactant, 35-55% by weight of PVA, and 9-10% by weight of
24 a cross-linking agent. The mounting layer can consist of

1 90% by weight of PVA and 10% by weight of the cross linking
2 agent.

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4 Just as the shape of the mold defines the form of the
5 product being molded during conventional molding, various
6 geometric inscriptions incorporated into the mold produce
7 various geometric surfaces upon the surface of the pad
8 substrate, enhancing the ability of the substrate to polish
9 highly finished surfaces. A pattern placed onto the
10 surface of various polishing pads imparts specific
11 polishing characteristics when polishing silicon wafer
12 substrates.

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14 Each of the reaction mixtures of the invention is
15 capable of being fortified with additives prior to reaction
16 molding for affecting the physical characteristics of the
17 resulting substrate. For instance, selected quantities
18 cutting and polishing agents such as aluminum oxide, cerium
19 oxide, carborundum, silicon dioxide and the like can be
20 added, either individually or in selected combinations, for
21 producing substrates having desired polishing
22 characteristics. In order to increase modulus and/or
23 reduce the coefficient of expansion, selected quantities of
24 one or more other fillers can be incorporated into the

1 reaction mixture such as microfibers, mineral fillers, etc.
2 Other suitable fillers include, but are not limited to,
3 various inorganic compounds such as silicon carbides, boron
4 derivatives, dry-type slurry materials, etc.

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6 In addition to the unique manner in which the pad
7 substrate of the invention is chemically made, micro-
8 asperities, which are basically controllable, can be
9 introduced into the reaction mixture to produce selected
10 surfaces, which are generally advantageous in polishing.
11 Preferably, the micro-asperities are in the form of micro
12 particles, which have the ability to transport or adsorb
13 charged particles during the polishing processes. This is
14 accomplished by adding to the reaction mixture a
15 hydroxylated polymer of PVA, which has been chemically and
16 molecularly altered to produce cationic, anionic,
17 amphoteric or neutral charges thereby affecting a charge
18 upon the surface of the medium to be polished. A plurality
19 of hydroxylated polymers can be added as well depending on
20 the charge that is desired to be affected on the surface of
21 the medium to be polished. This process of utilizing a
22 charged ion complex of PVA is taught in U.S. Letters Patent
23 No. 6,033,486, which is incorporated by reference herein.

1 Ultimately, the final physical properties of the
2 resulting substrate formed by the reaction of the reactants
3 in the mold depend largely on the reaction temperature, the
4 reaction pressure, and the duration of the reaction. The
5 reaction temperature can be varied or controlled in order
6 to affect the final physical properties as can the reaction
7 temperature and the reaction duration and any combination
8 of the foregoing can be altered, controlled or varied as
9 desired in any particular reaction event in order to affect
10 the final physical properties of the resulting substrate
11 including, but not limited to, hardness, hydrophilicity or
12 hydrophobic surface qualities, etc., and this will depend
13 on specific user needs. The molded substrate, which is a
14 polishing pad substrate, is, in accordance with the
15 principle of the invention, created by a chemical reaction
16 in a reaction mold, which eliminates the many steps
17 normally involved in producing conventional polishing pads.

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19 As previously mentioned, the shape of the mold in
20 which the reaction takes place, as with conventional
21 reaction molding techniques, governs the shape and form of
22 the resulting substrate of the invention. The shape and
23 form of the resulting substrate can be cylindrical, disc-
24 shaped, or any other desired shape in addition to any

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1 desired size, thickness, flatness, etc. It is important to
2 note that polishing pads are often required to have certain
3 surface characteristics in order to facilitate specific
4 polishing operations and to improve polishing performance.
5 Because the substrate of the invention is formed in a
6 reaction mold, the mold can be furnished with various
7 surface geometries for impartation to the resulting molded
8 substrate. The mold can embody a pattern and thus be a
9 patterned mold. By using a patterned mold, a pattern can
10 be imparted to the molded substrate in the course of the
11 reaction of the reaction mixture, which eliminates the
12 necessity of subsequently abrading the surface of the
13 resulting substrate in order to affect a particular pattern
14 to the surface of the substrate. As those of ordinary
15 skill will readily appreciate, patterned surfacing is often
16 important for polishing pads for channeling polishing
17 slurries during polishing and cleaning processes. Often, a
18 polishing pad having an extremely flat surface is required.
19 In this vein, the substrate of the invention can be
20 chemically molded in an electropolished reaction mold for
21 the purpose of imparting very flat or polished surfacing to
22 the resulting molded substrate.

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24 The reaction between adipic acid and urea is a

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1 condensation reaction that produces water. To determine
2 the amount of water produced in the reaction, a substrate
3 that is molded in accordance with the teachings of the
4 invention is removed from the reaction mold, as well as all
5 of the flash and cake that extruded out of the mold during
6 the reaction molding process. The flash and cake are
7 carefully weighed (constant weight), and subtracted from
8 the previously weighed mass of the charge (i.e., the
9 reactants) that was placed into the mold before raising the
10 temperature and pressure. The loss of weight represents
11 the weight of water produced by the reaction. Tables I and
12 II, below, shows these weight losses.

1 Table I. Reconciliation of the molding experiments for the
 2 production of polishing stones and polishing pads.

Date Molded	Reaction Type	Theoretical moles H ₂ O produced	Actual moles H ₂ O produced	Reagents	Remarks	
4/20/2001	Esterification	1.013	.8127	Adipic acid w/20%CeO ₂	W/20%CeO ₂	3
4/26/2001	Esterification	.417	.063	Adipic acid w/540S	W/15%CeO ₂	3
4/30/2001	Esterification	.97	.98	Adipic acid w/540S	W/0%CeO ₂	
5/2/2001	Esterification	.418	.128	Adipic acid w/540S	W/15%Al ₂ O ₃	3
5/3/2001	Esterification	.539	.127	Azelaic acid w/540S	W/20%Al ₂ O ₃	3
5/4/2001	Esterification	.458	.530	Azelaic acid w/540S	0% filler rubber like	1
5/9/2001	Esterification	.891	.653	Azelaic acid w/540S	W/16%Al ₂ O ₃	3
5/10/2001	Esterification	.402	.400	Adipic acid w/540S+urea	0% filler	2
5/10/2001	Urethanization	.453	.400	Adipic acid w/540S+urea		
5/19/2001	Urethanization	.341	.282	Adipic acid w/540S+urea	0% filler	
5/19/2001	Esterification	.301	.282	Adipic Acid w/540S+Urea	0% filler	
5/25/2001	Urethanization	.216	.190 A B	Adipic Acid w/540S+Urea	0% filler	
5/25/2001	Esterification	.216	.190 AB	Adipic Acid w/540S+Urea	0% filler	

3 Notes:

4 1-when hot, bounces like rubber.

5 2-urethanization probably did not occur, competing reaction was
 6 esterification.

7 3-filler absorbed water.

8 4-note A-type 4.0 -B reaction; note B-Mold "O" ringed water
 9 absorbed in cake.

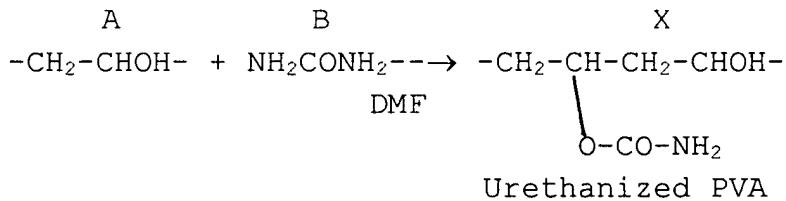
1 Table II. Cake mass reconciliation

Date Mold.	Mother mass date	(A) Mold chg. gm.	(B) Flash recovered gm.	(C) Cake mass gm.	A-B-C Net loss gm.	Normalized to moles H ₂ O
4/16/2001	4/5/2001	59.95	N/R	41.590	N/R	
4/18/2001	4/17/2001	60.00	N/R	34.9468	N/R	
4/19/2001	4/17/2001	71.04	N/R	44.4568	N/R	
4/20/2001	4/17/2001	72.02	19.906	37.6288	14.4852	.8127
4/23/2001	4/17/2001	72.12	14.07	41.3915	16.6585	.93
4/26/2001	4/26/2001	68.926	4.974	62.7352	1.2168	.063
4/30/2002	4/26/2001	70.079	4.090	48.3452	17.6438	.980
5/2/2001	4/26/2001	69.054	23.762	42.5881	2.841	.128
5/3/2001	5/3/2001	80.0078	26.680	50.8078	2.520	.127
5/4/2001	5/3/2001	72.246	8.175	54.4453	9.618	.530
5/7/2001	5/3/2001	82.635	N/R	N/R		
5/9/2001	5/8/2001	70.965	18.7294	40.4270	11.8086	.653
5/10/2001	5/9/2001	70.019	31.5638	30.6589	7.7963	.400
5/19/2001	5/9/2001	34.9758	24.274	24.274	5.0694	.282
5/25/2001	5/9/2001	25.0019	21.3591	21.3591	3.4159	.190

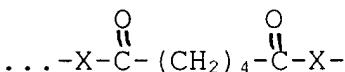
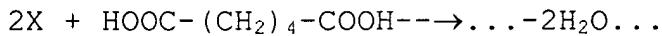
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1 Partially urethanized PVA is produced when urea is
2 reacted with PVA in a solvent of dimethylformamide (DMF),
3 examples of which are depicted below, namely, Example 1 and
4 Example 2.

Example 1.



Example 2.



... (Adipic Acid) - (X) - (Adipic Acid) - (X) ... (Adipic Acid) - X -
...

21 A study of the amino derivatives in examples 1 and 2
22 shows that a number of compounds are capable of being
23 produced that have extremely tough properties. However,
24 the problem with the derivatives is the fact that the amine
25 groups as well as the free hydroxyl groups on the PVA
26 molecule make the final product hydrophilic. To overcome
27 this problem, dibasic acid, whether adipic acid or other
28 dibasic acids, are used to insolubilize the urethanized
29 PVA.

1 It may not be necessary to react the materials in
2 Examples 1 and 2 at atmospheric temperature and pressure,
3 but rather at higher temperatures and pressures. The
4 advantage of such a scheme is that the use of DMF as a
5 solvent can be eliminated, since the latter is highly
6 toxic. Eliminating DMF makes the process environmentally
7 benign.

8

9 To test this theory, a mold was machined from
10 stainless steel, with a close fitting male closure. The
11 closure had machined into the side-walls two grooves for
12 the purpose of adding two "O" rings which would make the
13 mold air tight. The tests were conducted with and without
14 "O" rings. The purpose of eliminating the "O" rings was to
15 allow flash and steam to escape from the mold at higher
16 temperatures and pressures. The escapement of water as
17 steam permitted the analysis of the weight loss of the
18 reactants as a function of water produced by the reaction.
19 As water was lost, the pressure dropped, which necessitated
20 a constant monitoring of the press for the purpose of
21 retaining a constant pressure. This was accomplished by
22 continuously adjusting the ram pressure of the press to the
23 reactants pressure within the mold. In this fashion, the
24 mold pressure was held reasonably constant.

1 When the "O" rings were placed on the mold closure,
2 the water produced by the reaction was retained in the
3 final product. This is clearly seen in the Examples of
4 5/25/01 of Table I.

5

6 A second consideration is the impact of fillers upon
7 the reaction of the invention. This too is clearly seen in
8 Table I where inert fillers absorb the water produced,
9 illustrating a large discrepancy between the theoretical
10 amount of water calculated and that which was actually
11 detected.

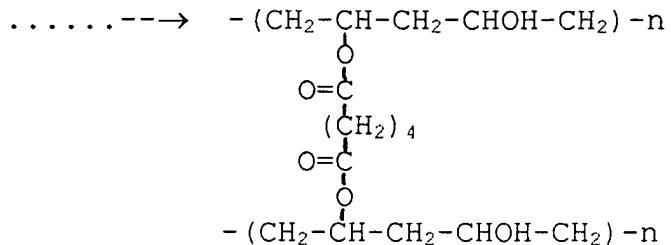
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13 When binary mixtures are reacted such as adipic acid
14 and PVA, the results are quite instructive. The reactions
15 become more complex when a tertiary reaction takes place
16 between three components. Binary reactions as described
17 above always result in esterification of PVA. The
18 preferred procedure is to urethanize the PVA with urea
19 first, then transfer the resulting derivative and mix with
20 the tertiary component, as in this case being a dibasic
21 acid such as adipic or azelaic acid.

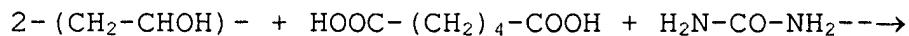
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23 When all three components are reacted together a
24 series of derivatives are produced, which are illustrated

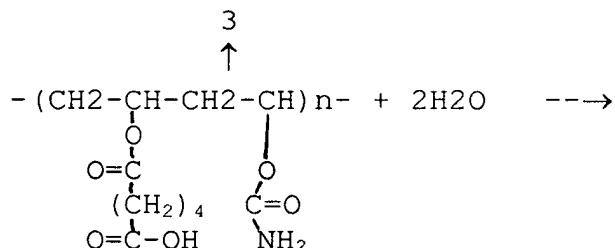
Example 5. Full-esterification.



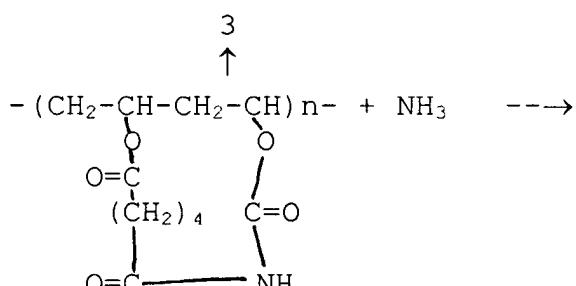
Example 6. Secondary high pressure reactions-half ester, half urethanized PVA.



Type A-



Type B-



36 Note: The hydroxide located at the "3" position of the PVA
37 molecule may not cleave at this point. Nevertheless, such
38 a structure is consistent with the recovered water produced
39 by this reaction.

40

41 And so a chemically homogenous polishing pad

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1 substrate, embodying the principle of the invention, is
2 created by a single chemical reaction as disclosed,
3 eliminating the many steps in producing conventional
4 polishing pads. With the invention, polishing pad
5 substrates can be directly molded in situ. The homogeneity
6 of the resulting substrate is due to the premixing of the
7 reaction constituents to produce a homogenous reaction
8 mixture. Because the resulting substrate is homogenous,
9 there are no multiple domains within the substrate to
10 produce layers of unpredictability as to phase composition
11 or separation. In accordance with the invention, the
12 reaction takes place in such a manner that the final
13 formulation or composition of the resulting substrate can
14 be controlled in order to produce a particular type of
15 substrate composition and substrate surface. The described
16 process produces an accurate, reproducible,
17 stoichiometrically-predictable substrate, which is not
18 possible with the conventional processes used to
19 manufacture needled felt based polishing pads saturated
20 with urethane derivatives or other polymers. Conventional
21 processes rely on saturation coating applications of fiber
22 like bases, which by their inherited natures, disperse the
23 coating and saturation chemicals in a heterogeneous manner,
24 producing irregular compositions and irregular and

1 unpredictable dispersions of the polymers. Prior art
2 methods of constructing polishing pads cause variations to
3 exist from pad to pad, making their reliability and
4 predictability of quality and performance undependable.

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6 The described process of reaction molding a polishing
7 pad substrate with a reaction mixture of a dibasic acid,
8 urea and PVA has, in addition to those already noted, many
9 important advantages. The reaction molding process of the
10 invention does not rely on a flowable material being forced
11 into a mold or enclosure to bond to a pre-inserted material
12 in the mold after it has been solidified. A polishing pad
13 produced by the process of the invention does not require
14 reinforcement, as described in conventional reaction
15 injection molding and other molding processes, to provide
16 structural integrity of the product. A polishing pad
17 produced by the process of the invention is also very
18 homogeneous, which allows the molding of a polishing pad in
19 a thickness not normally associated with conventional
20 processes and allows the surface of the pad to be
21 repeatedly re-textured or resurfaced with conventional
22 dressing tools. Unlike conventional polishing pad
23 production methods, the invention does not exploit
24 isocyanates, which are environmentally dangerous and toxic.

1 Polyvinyl alcohol, urea and most dibasic acids are not
2 toxic and are considered environmentally benign. The
3 process of the invention also may or may not require a
4 catalyst to drive the reaction process or employ toxic and
5 environmentally harmful polar solvents, and is very
6 efficient as it takes from one to three hours to complete
7 the reaction process and form a substrate. After a
8 substrate that is formed by the process of the invention is
9 removed from the mold, no subsequent curing, machining and
10 dressing are required.

11
12 A substrate formed by the process of the invention is
13 easily removed from the reaction mold, and it is not
14 necessary to treat the reaction mold with mold release
15 agents prior to the reaction process. The durometer or
16 hardness of a substrate formed by the process of the
17 invention is controllable by controlling the stoichiometric
18 relations of the reactants of the reaction mixture as well
19 as the reaction temperature, reaction time and reaction
20 pressure of the reaction, as monitored by the moles of
21 water produced during the reaction.

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23 Polishing pad substrates are directly molded in situ
24 with the invention. The addition of filler material helps

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1 to retain water in the pad, creating a hydrophilic surface.
2 Esters or amides can be produced by the process of the
3 invention, the polyesters being softer than the amides.
4 The use of closed O-ringed molds captures almost all of the
5 water produced in the condensation reaction of the
6 invention. Filler material can also be used to behave as
7 dry-slurries during the planarization process. Substrates
8 without filler material show a close correlation to
9 theoretical and actual results in the condensation data
10 presented above.

11

12 The present invention is described above with
13 reference to a preferred embodiment. However, those
14 skilled in the art will recognize that changes and
15 modifications may be made in the described embodiments
16 without departing from the nature and scope of the present
17 invention. Various changes and modifications to the
18 embodiment herein chosen for purposes of illustration will
19 readily occur to those skilled in the art. To the extent
20 that such modifications and variations do not depart from
21 the spirit of the invention, they are intended to be
22 included within the scope thereof.

1 Having fully described the invention in such clear and
2 concise terms as to enable those skilled in the art to
3 understand and practice the same, the invention claimed is:

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